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(54) **Thermoplastic acrylic resin composition**

(57) A thermoplastic acrylic resin composition comprises 20 to 98% by weight of a thermoplastic acrylic resin (A) composed solely of methyl methacrylate units or comprised of at least 80% by weight of methyl methacrylate units and 20% by weight or less of at least one kind of alkyl acrylate units in which the alkyl group has 1 to 4 carbon atoms, and 2 to 80% by weight of an acrylic particulate composite (B), the composition having a microstructure defined by the appearance of thin slices in an electron transmission microscope after staining with ruthenic acid and being defined by the composition of acetone-soluble/insoluble fractions. The composition has excellent transparency, impact resistance, weather resistance and stress whitening resistance, and is also low in temperature dependence of haze.

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THERMOPLASTIC ACRYLIC RESIN COMPOSITION

1 BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to a thermoplastic acrylic resin composition. More particularly, it relates to a thermoplastic acrylic resin composition which has excellent transparency, impact resistance, weather resistance and stress whitening resistance and is also low in temperature dependence of haze.

RELATED ART

10 It is common to improve impact resistance of thermoplastic resin by means of introducing an elastomeric substance into the resin. Diene elastomers are generally used for this purpose, but employment of such diene elastomers in resin products designed for outdoor use is undesirable because of the poor weather resistance property of diene elastomers.

Many studies have been made on the use of acrylic elastomers to provide impact resistance to the resin compositions without affecting their weather resistance property. Especially, many proposals involving the use of acrylic polymers having a multi-layer structure, have been made.

For example, there have been proposed the blending of a particulate composite of a 3- or 4-layer structure and a thermoplastic polymer to improve impact

25

- 1 resistance without impairing transparency (Japanese
Patent Publication No. 27576/80); use of an acrylic
polymer which is basically of a three-layer structure
and has, between every adjoining layers, an intermediate
5 layer having a concentration gradient which varies at
an almost constant rate (Japanese Patent Application
Kokai (Laid-open) Nos. 129449/76 and 58554/78);
a polymer which is basically composed of three main
layers and has at least one intermediate layer between
10 the central soft layer and the outermost layer (Japanese
Patent Publication No. 36646/84 and Japanese Patent
Application Kokai No. 147539/82); a polymer having a soft-
hard-soft-hard four-layer structure (Japanese Patent
Application Kokai No. 94947/80). These proposals are
15 certainly effective for improving anti-stress-blushing
qualities but have the problems in transparency and/or
whitening, high temperature dependence of haze.

There have also been proposed a method in which
in the course of polymerization of the second layer (soft
20 layer), at a point when the polymerization rate has
reached 60 to 90% by weight, the monomer mixture for the
third layer (hard layer) is added and polymerized
(Japanese Patent Application Kokai No. 202213/84), and a
method in which the monomer mixture forming the second
25 layer (soft layer) is partly (15 to 30% by weight) left
unreacted, and the third layer monomer mixture is
polymerized to thereby form a layer structure which
gradually changes in composition (Japanese Patent

- 1 Application Kokai No. 27516/88). These methods are capable of improving impact resistance and weathering resistance but are unable to provide good transparency to the composition.
- 5 As seen from above, mass proposals have been made on the particulate composites having a multi-layer structure for the purpose of improving the defective properties of acrylic resins without impairing their favorable characteristics. These proposals have indeed
- 10 provided considerable improvements on transparency, anti-stress-whitening qualities and mechanical strength, but in regard to temperature dependence of haze, no satisfactory result was obtained.

SUMMARY OF THE INVENTION

The present inventors have made extensive studies for improving the transparency and lowering temperature dependence of haze of impact-resistant acrylic resin compositions and, as a result, have found that useful properties can be attained by using an acrylic particulate composite having a specific molecular

1 structure. This finding has led to the obtainment of
the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides a thermoplastic
5 acrylic resin composition comprising 20 to 98% by weight
of a thermoplastic acrylic resin (A) which is composed
solely of methyl methacrylate units or comprised of at
least 80% by weight of methyl methacrylate units and
20% by weight or less of at least one kind of alkyl
10 acrylate units, in which the alkyl group has 1 to 4
carbon atoms, and 2 to 80% by weight of an acrylic
particulate composite (B), characterized in that when a
ruthenic acid-stained ultra-thin section of said
composition is observed under a transmission electron
15 microscope,

(a) said composition has an island-and-sea
structure, and the dispersoid constituting the island
has a multi-layer structure consisting of concentric
outer layer portions (α layer) stained with ruthenic
20 acid and inner layer portion (β layer) not stained with
ruthenic acid,

(b) said inner layer portion (β layer) not
stained with ruthenic acid has dispersed therein micro-
scopically a multitude of portions stained with ruthenic
25 acid (γ layer), and

(c) the average particle size of said β layer
is 1,500 to 2,500 Å, the average thickness of the α layer

1 surrounding said β layer is 250 to 400 Å, and the average
particle size of the island as a whole is 2,000 to 3,000 Å,
and when said thermoplastic acrylic resin composition is
fractionated with acetone,

5 (d) the portion soluble in acetone occupies 30
to 98% by weight of the composition and comprises 80 to
100% by weight of methyl methacrylate units, 0 to 20%
by weight of alkyl acrylate units, in which the alkyl
group has 1 to 8 carbon atoms, and 0 to 20% by weight of
10 vinyl monomer units copolymerizable therewith, and

(e) the portion insoluble in acetone is 2 to
70% by weight and comprises 20 to 70% by weight of methyl
methacrylate units, 10 to 75% by weight of alkyl acrylate
units, in which the alkyl group has 1 to 8 carbon atoms,
15 and 2 to 30% by weight of vinyl monomer units copolymer-
izable therewith, wherein the swelling index of said
acetone-insoluble portion in methyl ethyl ketone is
1.5 to 6, and the tensile modulus is 1,000 to 10,000
kg/cm².

20 The thermoplastic acrylic resin (A) in the
present invention can be obtained by polymerizing methyl
methacrylate alone or by copolymerizing methyl methacrylate
with 20% by weight or less of an alkyl acrylate, in which
the alkyl group has 1 to 4 carbon atoms, by a conventional
25 method.

In the preparation of said thermoplastic
acrylic resin (A), the monomeric materials other than
methyl methacrylate, such as alkyl methacrylate, wherein

1 the alkyl has at least 2 carbon atoms, styrene, styrene
derivatives, acrylonitrile, methacrylonitrile, etc.,
may be copolymerized in small quantities within the
limits not prejudicial to the transparency or impact
5 resistance of the composition.

The acrylic particulate composite (B) in the
present invention is comprised of methyl methacrylate,
an alkyl acrylate in which the alkyl group has 1 to 8
carbon atoms, a vinyl monomer copolymerizable therewith
10 used for the purposes of adjusting refractive index,
etc., a polyfunctional crosslinking agent and a
polyfunctional grafting agent.

The acrylic particulate composite (B) can be
produced by means of sequential multi-stage polymeriza-
15 tion. The preferred method of polymerization is emulsion
polymerization. Other methods are available for
producing said composite (B). For instance, it can be
produced by an emulsion-suspension polymerization method
in which emulsion polymerization is converted into a
20 suspension system during polymerization of the outermost
layer.

Examples of said alkyl acrylate, in which the
alkyl group has 1 to 8 carbon atoms are methyl acrylate,
ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate
25 and the like. The most preferred is n-butyl acrylate.

Examples of aromatic vinyl compounds usable
in the preparation of said composite (B) are styrene and
substituted styrene derivatives. Styrene is preferred.

1 As said polyfunctional crosslinking agent,
there can be used the generally known types of cross-
linking agents such as divinyl compounds, diallyl
compounds, diacrylic compounds and dimethacrylic
5 compounds. A polyethylene glycol diacrylate having a
molecular weight of 200 to 600 of diacrylic compounds
is most preferably used.

 As said polyfunctional grafting agent, there
can be used polyfunctional monomers having different
10 functional groups, such as allyl esters of acrylic acid,
methacrylic acid, maleic acid, fumaric acid and the
like. Allyl methacrylate is preferred.

 The thermoplastic acrylic resin composition
of this invention has a specific structure typified by
15 the facts that as noted when a ruthenic acid-stained
ultra-thin section of said composition is observed under
a transmission type electron microscope,

 (a) said composition has an island-and-sea
structure, and the dispersoid constituting the island
20 has a multi-layer structure comprising concentric outer
layer portions (α layer) stained with ruthenic acid and
an inner layer portion (β layer) not stained with
ruthenic acid,

 (b) said inner layer portion (β layer) not
25 stained with ruthenic acid has dispersed therein micro-
scopically a multitude of portions stained with ruthenic
acid (γ layer), and

 (c) the average particle size of said β layer

1 is 1,500 to 2,500 Å, the average thickness of the α layer
surrounding said β layer is 250 to 400 Å, and the average
particle size of the island as a whole is 2,000 to
3,000 Å.

5 Such a specific molecular structure of the
composition is considered conducive, to characterize the
composition with a remarkable improvement of transparency
and temperature dependence of haze without affecting the
properties which are specific to acrylic resin, such as
10 impact resistance, anti-stress-whitening qualities and
weather resistance.

 This could hardly be anticipated from the
hitherto proposed multi-layer structured polymers.

 The facts have been noted that if the inner
15 layer portion (β layer) not stained with ruthenic acid,
is not surrounded with the outer layer portion (α layer)
stained with ruthenic acid, the obtained composition is
poor in mechanical strength such as impact resistance,
and if the inner layer portion (β layer), not stained
20 with ruthenic acid, has not dispersed therein micro-
scopically a multitude of portions (γ layer) stained
with ruthenic acid, the resulting composition is poor
in impact strength or unsatisfactory in transparency and
temperature dependence of haze.

25 It is essential in the present invention that
the β layer has an average particle size of 1,500 to
2,500 Å. When its average particle size is less than
1,500 Å, the obtained composition proves to be poor in

1 transparency and temperature dependence of haze, and when
said average particle size exceeds $2,500 \text{ \AA}$, the composition
is reduced in impact resistance.

The α layer surrounding the β layer needs to
5 have an average thickness of 250 to 400 \AA , preferably
300 to 400 \AA . When the average thickness of the α layer
is less than 250 \AA , the composition produced is poor in
impact resistance, and when it exceeds 400 \AA , the
composition becomes unsatisfactory in transparency and
10 temperature dependence of haze.

When the average particle size of the island as
a whole is less than $2,000 \text{ \AA}$, the composition produced is
found to be poor in impact resistance, and when it
exceeds $3,000 \text{ \AA}$, the obtained composition is poor in
15 transparency.

When the prepared thermoplastic acrylic resin
composition is fractionated with acetone, if the portion
soluble in acetone is less than 30% by weight, said resin
composition is found to be poor in moldability and color
20 tone, and if said portion exceeds 98% by weight, the
resin composition is poor in impact resistance. In the
thermoplastic acrylic resin composition of this invention,
it is necessary that the portion soluble in acetone is
of a composition which comprises 80 to 100% by weight
25 of methyl methacrylate units, 0 to 20% by weight of alkyl
acrylate units, in which the alkyl group has 1 to 8
carbon atoms, and 0 to 20% by weight of vinyl monomer
units copolymerizable therewith. Departure from the

1 above-defined ranges of the respective compositional
units leads to an undesirable result in weather
resistance or transparency. Examples of said copolymer-
izable vinyl monomers are alkyl methacrylate, in which the
5 carbon number of alkyl group is 2 to 4, styrene, styrene
derivatives, acrylonitrile, methacrylonitrile and the
like.

On the other hand, it is necessary that the
portion which is insoluble in acetone is comprised of
10 20 to 70% by weight of methyl methacrylate units, 10
to 75% by weight of alkyl acrylate units, in which the
alkyl group has 1 to 8 carbon atoms, and 2 to 30% by
weight of vinyl monomer units copolymerizable therewith.
Departure from the above-defined ranges results in
15 unsatisfactory impact resistance and transparency.
Examples of vinyl monomers usable here are alkyl
methacrylate, in which the number of carbon atoms
contained in the alkyl group is 2 to 4, styrene, styrene
derivatives, acrylonitrile, methacrylonitrile and the
20 like.

In the thermoplastic acrylic resin composition
according to the present invention, it is also necessary
that the portion insoluble in acetone has a swelling
index of 1.5 to 6, preferably 2 to 4.5 in methyl
25 ethyl ketone. The composition of this invention is also
required to have an elastic tensile modulus of 1,000
to 10,000 kg/cm², preferably 2,000 to 6,000 kg/cm².
If said elastic modulus is outside said range, the

1 composition becomes unsatisfactory in impact resistance,
transparency and temperature dependence of haze.

For the preparation of acrylic particulate composite (B) of this invention, it is advantageous to
5 use an emulsion polymerization method as previously stated. Polymerization temperature suited for forming the polymer or copolymer is selected from the range of 30 to 120°C, preferably 50 to 100°C for each layer. For forming such a multi-layer structured polymer, it is expedient
10 to use a so-called seed polymerization method according to which it is possible to form said polymer by adding and reacting stepwise the respective monomers or monomer mixtures. When carrying out the polymerization for forming the second and succeeding layers, it is necessary
15 to select the conditions that will not allow the formation of new particles. This can be accomplished by adjusting the amount of emulsifier used so that it will not exceed the critical micell concentration. Formation or non-formation of new particles can be confirmed by
20 observation with an electron microscope.

For adjusting the average thickness of α layer and the average particle size of β layer to the prescribed levels, it is important to properly select the amount (parts by weight) of monomer mixture, monomer/water
25 ratio by weight, and the type and the amount of emulsifier used for each layer.

For effecting microscopic dispersion of a multitude of portions stained with ruthenic acid

- 1 (γ layer) in the inner layer portion not stained with
ruthenic acid (β layer), it is imperative to adequately
select the composition of the β layer, its molecular
weight, crosslinking density and distance between the
5 crosslinking points and to also properly select the
composition and feed of the monomer mixture constituting
the portion stained with ruthenic acid.

- The polymerization initiator used in the above
process is not subject to any specific restrictions;
10 it is possible to use conventional inorganic type
initiator such as water-soluble persulfate, perborate,
etc., singly or it may be used in combination with a
sulfite, thiosulfate or the like to form a redox type
initiator. It is also possible to use such redox type
15 initiators as oil-soluble organic peroxide/ferrous
salt mixture, organic peroxide/sodium sulfoxylate mixture
and the like.

- The acrylic particulate composite (B) having a
specific structure obtained according to the above-
20 described polymerization method can be worked into a
particulate solid from the state of polymer latex by
subjecting it to such treatments as salting-out,
coagulating washing, drying, etc., by the known methods.

- The thermoplastic acrylic resin composition
25 of this invention can be obtained by melting and
kneading 2 to 80% by weight of the thus obtained acrylic
particulate composite (B) and 20 to 98% by weight of the
thermoplastic acrylic resin (A). The thermoplastic

1 acrylic resin used herein may be one that was obtained
according to any of the known polymerization methods
such as bulk polymerization, solution polymerization,
suspension polymerization, emulsion polymerization, etc.
5 When the content of acrylic particulate composite (B)
is less than 2% by weight, the obtained composition
lacks impact resistance, and when its content exceeds
80% by weight, the polymer produced is dull in
color tone.

10 In the course of kneading in the production
of the composition of this invention, there can be added
a stabilizer, lubricant, dye, pigment and/or other
additives as required.

The composition of this invention obtained in
15 the manner described above can be injection or extrusion
molded into an article having excellent transparency and
impact resistance and also low in temperature dependence
of haze.

EXAMPLES

20 The present invention will be hereinafter
described in further detail by showing the examples
thereof, but it is to be understood that these examples
are merely intended to be illustrative and not to be
construed as limiting the scope of the invention. In
25 the Examples and Comparative Examples described below,
measurements and determinations were made by using the
following methods or apparatus.

1 Haze

Haze of 3 mm thick specimens is measured by using an integrating-sphere haze meter at 23°C and 70°C.

The results are indicated by the following marks:

- 5 ⊙ : Haze is less than 10%.
 ○ : Haze is 10 to less than 20%.
 Δ : Haze is 20 to less than 30%.
 X : Haze is 30% or above.

Preparation of specimens for electron microscopy

- 10 Ultra-thin sections (slices) of smaller than 0.5 mm² are formed and their surfaces are cut and finished by using a diamond knife. Each of the thus prepared specimens is placed in a hermetically sealed light-shielded container and exposed therein to vapors
15 of a 1% ruthenic acid solution for several hours and stained.

Average particle size and average thickness

- A transmission type electron microphotograph (100,000X magnification) of an ultra-thin section (sample)
20 sliced from a molded article and stained with ruthenic acid is prepared, then 100 particles in the microphotograph are selected at random and their diameter is measured. The arithmetic mean of 100 measurements is given here as average particle size (diameter). In the
25 case of the particles which could not be regarded as spherical, the diameter along the major axis and the diameter along the minor axis are measured and their arithmetic mean is given as particle diameter. As for

- 1 the average thickness, it is determined by following the
similar procedure, that is, 100 particles are picked
out at random, their thickness is measured, and the
arithmetic mean of 100 measurements is given as an
5 average thickness. When the thickness of a particle is
non-uniform, its greatest thickness and smallest
thickness are measured and their arithmetic mean is
reckoned as the thickness of the particle.

Fractionation with acetone

- 10 Approximately 1.00 g of pellets are precisely
weighed (W_1) and 30 ml of acetone is added thereto.
The solution is shaken at 25°C for 5 hours and then
centrifuged at 23,000 r.p.m. and 5°C for 30 minutes.
After removing the supernatant (a) by decantation, 30 ml
15 of acetone is freshly added and the solution is shaken
at 25°C for one hour and then centrifuged at 23,000
r.p.m. and 5°C for 30 minutes. After removing the
supernatant (b) by decantation, the residue is dried
in vacuo at 100°C for 2 hours, then cooled to room
20 temperature in a desiccator and the residue weight (W_2)
is measured. The acetone insoluble matter is calculated
in wt% from the following formula:

$$\text{Acetone insoluble matter} = \frac{W_2}{W_1} \times 100 \quad (\text{wt}\%)$$

Swelling index

- 30 ml of methyl ethyl ketone is added to
25 approximately 0.5 g of pellets, and after 24-hour

1 immersion at 25°C, the solution is shaken for 5 hours
and then centrifuged at 18,000 r.p.m. and 5°C for one
hour. The supernatant is removed by decantation. Then
30 ml of methyl ethyl ketone is freshly supplied and the
5 solution is shaken at 25°C for one hour and then
centrifuged at 18,000 r.p.m. and 5°C for one hour.
After removing the supernatant, the residue is weighed
(W₃). Then the residue is dried in vacuo at 100°C for
2 hours and weighed (W₄). The degree of swelling is
10 calculated from the following equation:

$$\text{Swelling index} = \frac{W_3 - W_4}{W_4}$$

Compositional analysis

As for the acetone soluble matter, the
supernatants (a) and (b) obtained from fractionation with
acetone are poured into a large amount of methanol, and
15 as to the acetone insoluble matter obtained by drying
the precipitate in vacuo, there are used the samples
obtained from acetone fractionation. Compositional
analysis of each sample is performed by pyrolysis gas
chromatography.

20 Tensile modulus

The insoluble matter obtained from acetone
fractionation is compression molded at 150°C to form
a film, and test pieces measuring 15 ± 0.5 mm in width,
0.50 ± 0.05 mm in thickness and 70 ± 1 mm in length are

1 prepared therefrom. Each test piece is subjected to a
tensile test at a pulling rate of 50 mm/min by setting
the chuck interval at 50 mm.

The following abbreviations are used for the
5 compounds in the Examples and Comparative Examples:

MMA: methyl methacrylate

BA: n-butyl acrylate

St: styrene

MA: methyl acrylate

10 ALMA: allyl methacrylate

PEGDA: polyethylene glycol diacrylate (Mw = 200 or
600)

n-OM: n-octylmercaptan

HMBT: 2-(2'-hydroxy-5'-methylphenyl)benzotriazole

15 EXAMPLE 1

6,000 ml of ion exchange water and 12 g of
sodium dihexylsulfosuccinate are supplied into a 10-liter
reactor having a reflux condenser. The mixture in the
reactor was stirred at 250 r.p.m. and heated to 70°C
20 under a nitrogen atmosphere to create a situation which
is substantially free from the influence of oxygen.
After the addition of 1.6 g of ammonium persulfate, a
mixture (B1) consisting of 592 g of MMA, 39 g of BA,
0.16 g of HMBT and 1.6 g of ALMA is continuously added
25 over a period of 60 minutes. Thereafter, the mixture is
allowed to stand for 30 minutes. The thus produced
polymer latex is cooled to 40°C, 32 g of St is added

1 and stirred for 60 minutes. Then a mixture (B2) consisting of 128 g of BA, 0.08 g of HMBT, 1.6 g of ALMA and 1.6 g of PEGDA (Mw = 200) is added, followed by further stirring for 60 minutes.

5 The resulting latex was heated to 70°C and 1.6 g of ammonium persulfate is added, after which a mixture (B3) consisting of 576 g of BA, 144 g of St, 0.24 g of HMBT, 7.2 g of ALMA and 7.2 g of PEGDA (Mw = 200) is continuously added over a period of 100 minutes
10 and then the total blend is allowed to stand for 60 minutes.

 Then a mixture (B4) consisting of 179 g of BA, 45 g of St, 224 g of MMA, 0.08 g of HMBT, 2.4 g of ALMA and 2.4 g of PEGDA (Mw = 200) is continuously
15 added over a period of 60 minutes, and the blend is allowed to stand for 60 minutes.

 Lastly, a mixture (B5) consisting of 400 g of MMA, 32 g of BA, 1.2 g of n-OM and 0.08 g of HMBT is continuously added over a period of 20 minutes, and
20 the blend of the mixtures is allowed to stand for 30 minutes, then heated to 95°C and maintained in this state for one hour.

 The thus prepared latex is added to a hot 3 wt% aqueous solution of sodium sulfate for effecting
25 salting-out and coagulation, and after repeated dehydration and washing, the product is dried to obtain a particulate composite (B).

 20 parts by weight of this particulate

1 composite (B) is mixed with 80 parts by weight of a
MMA-MA copolymer (MMA : MA (weight ratio) = 97.5 : 2.5;
 $\eta_{sp}/C = 0.54$ dl/g (measured in a 0.30 g/dl chloroform
solution at 25°C), and the mixture is pelletized at
5 240°C by using a 30 mm ϕ double-screw extruder having a
vent (Model A manufactured by Nakatani Machinery Co.,
Ltd.). The pellets are molded into a prescribed test
specimen by using an in-line screw injection molding
machine (Model IS-75S manufactured by Toshiba Machinery
10 Co., Ltd.) operated under the conditions of molding
temperature = 250°C, injection pressure = 900 kgf/cm²
and mold temperature = 50°C, and the test specimen is
subjected to determination of properties. The obtained
resin composition is excellent in transparency and
15 temperature dependence of haze and also has high impact
resistance.

An ultra-thin section stained with ruthenic
acid is prepared from said test specimen and observed under
a transmission electron microscope. It was found that
20 the average particle size of the β layer not stained with
ruthenic acid is 2,300 Å, the average particle size of
the island as a whole is 3,000 Å, the average thickness
of the α layer stained with ruthenic acid is 350 Å, and
the portion not stained with ruthenic acid has dispersed
25 therein microscopically a multitude of portions (γ layer)
stained with ruthenic acid.

When the pellet is fractionated with acetone,
it has 18.5% of acetone insoluble matter. The swelling

- 1 index in methyl ethyl ketone is 3.5. The tensile
modulus of the film prepared from the acetone insoluble
matter is 3,300 kg/cm².

The result of compositional analysis by

- 5 pyrolysis gas chromatography showed that the acetone
soluble matter is comprised of 97.3 wt% of MMA, 2.3 wt%
of MA and 0.4 wt% of BA, while the acetone insoluble
matter comprised 40 wt% of MMA, 47 wt% of BA and 13 wt%
of St.

10 EXAMPLE 2

- The procedure of Example 1 is followed except
that the mixture (B1) is composed of 312 g of MMA,
249 g of BA, 62 g of St, 0.16 g of HMBT and 1.6 g of
ALMA, and that PEGDA with a molecular weight of 200 is
15 replaced with the equal amount of a PEGDA with a
molecular weight of 600.

EXAMPLE 3

- The procedure of Example 1 is followed except
that the mixture (B1) is composed of 928 g of MMA, 56 g
20 of BA, 0.24 g of HMBT and 2.4 g of ALMA, that 29 g of
St is used as monomer to be added to the polymer latex
of 40°C and the mixture (B2) to be also added thereto
is composed of 122 g of BA, 0.09 g of HMBT, 1.3 g of
ALMA and 1.3 g of PEGDA (Mw = 600), that the continuously
25 added mixture (B3) is composed of 546 g of BA, 136 g of
St, 0.26 g of HMBT, 7.0 g of ALMA and 7.0 g of PEGDA

- 1 (Mw = 600), that no mixture (B4) is used, and that the mixture (B5) is composed of 600 g of MMA, 48 g of BA, 1.84 g of n-OM and 0.16 g of HMBT.

EXAMPLE 4

- 5 The procedure of Example 1 is followed except that 44 g of St is used as the monomer to be added to the polymer latex at 40°C and the mixture (B2) to be also added thereto is composed of 178 g of BA, 0.07 g of HMBT, 2.2 g of ALMA and 2.2 g of PEGDA (Mw = 600), that
10 the continuously added mixture (B3) was composed of 659 g of BA, 165 g of St, 0.22 g of HMBT, 8.2 g of ALMA and 8.2 g of PEGDA (Mw = 600), that no mixture (B4) is added, and that the mixture (B5) is composed of 600 g of MMA, 48 g of BA, 1.8 g of n-OM and 0.16 g of
15 HMBT.

EXAMPLE 5

- 6.860 ml of ion exchange water and 17.2 g of sodium dihexylsulfosuccinate are supplied into a reactor similar to that used in Example 1, and the
20 mixture is stirred at 250 r.p.m. and heated to 75°C under a nitrogen atmosphere.

- A mixture consisting of 534.6 g of MMA, 19.4 g of BA, 0.443 g of ALMA and 0.166 g of HMBT is divided into two portions which are 2 : 3 in weight ratio, and
25 the former (smaller) portion is designated as mixture (B1) and the latter (larger) portion as mixture (B2).

1 Mixture (B1) is added to the reactor, and 5
minutes thereafter, 0.22 g of ammonium persulfate is
added, the mixed solution being allowed to stand for
45 minutes. Then mixture (B2) is continuously added
5 over a period of 12 minutes, and the blend is allowed
to stand for 20 minutes.

The resultantly obtained polymer latex is
cooled to 40°C.

Then a mixture consisting of 1,141 g of BA,
10 259 g of St, 3.64 g of PEGDA (Mw = 200), 14.84 g of
ALMA and 0.42 g of HMBT is divided into 5 : 1 (in
weight ratio) portions, and the former (larger) portion
is designated as mixture (B3) and the latter (smaller)
portion as mixture (B4). Also, a mixture consisting of
15 876.1 g of MMA, 11.54 g of BA, 2.66 g of n-OM and
0.27 g of HMBT is divided into 1 : 1 (in weight ratio)
portions, one portion being designated as mixture (B5)
and the other portion as mixture (B6). Mixture (B3)
is added to the reactor and stirring is continued for
20 60 minutes. The resulting latex is heated to 75°C,
added with 0.89 g of ammonium persulfate and allowed
to stand for 190 minutes.

Then 0.53 g of ammonium persulfate is added
to the reactor, followed by the addition of mixture (B4)
25 at one time, and 2 minutes thereafter, the addition of
mixture (B5) is started, which addition lasts for 90
minutes without interruption. After this addition,
this blend of the mixtures is allowed to stand for 60

1 minutes.

Further, 0.18 g of ammonium persulfate is added to the reactor, and lastly mixture (B6) is added over a period of 20 minutes, followed by a 30-minute
5 standing period. Then the total mixture is heated to 95°C and kept in this state for 60 minutes.

The latex thus obtained is subjected to the same after-treatments, kneading, molding and evaluations as conducted in Example 1.

10 EXAMPLE 6

The procedure of Example 5 is followed except that the amount of sodium dihexylsulfosuccinate used is changed to 22.6 g, that the mixture consisting of 534.6 g of MMA, 19.4 g of BA, 0.443 g of ALMA and 0.166 g of
15 HMBT is not divided into (B1) and (B2), and after the lapse of 5 minutes from addition of 0.22 g of ammonium persulfate, said mixture is continuously added over a period of 45 minutes, and that after this addition, the blend is allowed to stand for 20 minutes.

20 The results of property evaluations of the test specimens in the above Examples are shown in Table 1.

COMPARATIVE EXAMPLE 1

The procedure of Example 3 is followed except
25 that mixture (B3) is composed of 236 g of BA, 56 g of St, 0.16 g of HMBT, 2.8 g of ALMA and 2.8 g of PEGDA

- 1 (Mw = 600), and that mixture (B5) is composed of 916 g
of MMA, 68 g of BA, 2.8 g of n-OM and 0.32 g of HMBT.

COMPARATIVE EXAMPLE 2

- The procedure of Example 3 is followed except
5 that mixture (B3) is composed of 236 g of BA, 56 g of
St, 0.16 g of HMBT, 2.8 g of ALMA and 2.8 g of PEGDA
(Mw = 600), and that mixture (B4) is composed of 316 g
of MMA, 20 g of BA, 0.16 g of HMBT and 3.4 g of ALMA.

COMPARATIVE EXAMPLE 3

- 10 6,860 ml of ion exchange water and 13.72 g
of sodium dihexylsulfosuccinate are supplied to a
reactor similar to that used in Example 1. The mixture
is stirred at 250 r.p.m. and heated to 70°C under a
nitrogen atmosphere.

- 15 Then 0.74 g of ammonium persulfate is added,
and 10 minutes thereafter, addition of mixture (B1)
consisting of 238 g of MMA, 16.3 g of BA and 0.64 g of
ALMA is started, which addition lasts for 10 minutes
without interruption. Thereafter, the blend of the
20 mixtures is allowed to stand for 30 minutes.

- After the above operation, 2.85 g of ammonium
persulfate is added, and after the lapse of 10 minutes
from its addition, mixture (B2) consisting of 1,443 g of
BA, 338 g of St and 18.9 g of ALMA is added, the
25 addition being continued for 140 minutes without
interruption, and then the blend of the mixtures is

1 allowed to stand for 150 minutes.

The above operation is followed by another addition of 1.22 g of ammonium persulfate and, 10 minutes thereafter, further addition of mixture (B3) consisting
5 of 718 g of MMA, 45.8 g of BA and 2.29 g of n-OM is continuously made over a period of 50 minutes, after which the blend of the mixtures is allowed to stand for 70 minutes.

The thus obtained latex is subjected to the
10 same after-treatments, kneading, molding and evaluations as carried out in Example 1.

COMPARATIVE EXAMPLE 4

The procedure of Comparative Example 3 is followed except that the period of time of addition of
15 mixture (B1) is 20 minutes, and that the total mixture was lastly heated to 95°C and maintained in this state for 60 minutes.

COMPARATIVE EXAMPLE 5

The procedure of Example 1 is followed except
20 that the amount of emulsifier added is 6 g, that the period of time of addition of mixture (B1) is 120 minutes, that mixture (B3) is composed of 748 g of BA, 187 g of St, 0.24 g of HMBT, 9.4 g of ALMA and 9.4 g of PEGDA (Mw = 600), that mixture (B5) is composed of 200 g of
25 MMA, 16 g of BA, 0.64 g of n-OM and 0.08 g of HMBT, and that PEGDA with a molecular weight of 200 used in each

1 mixture is changed to PEGDA with a molecular weight of
600.

The results of property evaluations of the
test specimens in the above Comparative Examples are
5 shown in Table 1.

It is evident from the results of Comparative
Examples that when the average thickness of α layer
stained with ruthenic acid is less than 250 Å, the
composition produced is poor in impact resistance, and
10 when said average thickness exceeds 400 Å, transparency
and temperature dependence of haze are deteriorated.

As seen from the above, when the blend departs
from the compositional ranges specified in the present
invention, a composition cannot be obtained which is
15 excellent in impact resistance, transparency and
temperature dependence of haze.

Table 1

		EXAMPLES					
		1	2	3	4	5	6
Form of dispersion	(1) Average particle size of β layer [Å]	2300	2400	1800	2100	1650	1540
	(2) Average thickness of α layer [Å]	350	300	260	400	370	320
	(3) Average particle size of island as a whole [Å]	3000	3000	2380	2900	2390	2180
	(4) Presence or absence of microscopically dispersed γ layers in β layer	Pre-sent	Pre-sent	Pre-sent	Pre-sent	Pre-sent	Pre-sent
Properties	Izod impact strength (kg·cm/cm)	4.4	4.2	3.5	4.5	4.3	3.9
	Haze	○	○	○	○	○	○
		○	○	○	○	○	○
Analysis of acetone insolubles	Acetone insolubles (wt%)	18.5	17.3	17.6	17.7	16.8	18.2
	Swelling index	3.5	3.4	2.9	2.7	2.8	2.7
	Tensile modulus (kg/cm ²)	3300	2500	6000	2000	2500	2400

- To be continued -

Table 1 (Cont'd)

Composi- tional analysis	Acetone solubles	MMA (wt%)	97.3	97.4	97.2	97.1	97.4	97.3
		MA (wt%)	2.3	2.3	2.0	2.3	2.4	2.3
	Acetone insolu- bles	BA (wt%)	0.4	0.3	0.8	0.6	0.2	0.4
		MMA (wt%)	40	26	52	33	40	40
		BA (wt%)	47	59	38	54	49	48
		ST (wt%)	13	15	10	13	11	12

- To be continued -

Marks	Haze
◎	less than 10%
○	10 to less than 20%
Δ	20 to less than 30%
×	30% or above

Table 1 (Cont'd)

COMPARATIVE EXAMPLES				
1	2	3	4	5
2280	2360	980	1200	2900
160	170	760	900	700
2600	2700	2500	3000	4300
Pre-sent	Pre-sent	Absent	Absent	Pre-sent
1.3	1.2	4.0	4.1	5.1
⊙	⊙	⊙	⊙	○
⊙	⊙	Δ	x	x
14.9	15.1	17.5	17.1	18.6
2.6	1.3	4.7	4.3	3.2
8710	9100	2200	2330	3000

97.1	97.2	97.2	97.2	97.4	97.4
1.8	2.0	2.0	2.0	2.5	2.5
1.1	0.8	0.8	0.8	0.1	0.1
68	74	38	39	40	40
27	22	58	58	48	48
5	4	4	3	12	12

1 According to the present invention, there is
provided an acrylic resin composition which is free of
the defects possessed by the conventional acrylic
particulate composites and which has excellent impact
5 resistance and temperature dependence of haze while
having good transparency and moldability which are
specific to acrylic resins.

CLAIMS

1. A thermoplastic acrylic resin composition comprising 20 to 98% by weight of a thermoplastic acrylic resin (A) composed solely of methyl methacrylate units or comprised of at least 80% by weight of methyl methacrylate units and 20% by weight or less of at least one kind of alkyl acrylate units in which the alkyl group has 1 to 4 carbon atoms, and 2 to 80% by weight of an acrylic particulate composite (B), characterized in that when an ultra-thin section sliced from said thermoplastic acrylic resin composition and stained with ruthenic acid is observed under a transmission electron microscope,

(a) said composition has an island-and-sea structure, and the dispersoid constituting said island has a multi-layer structure consisting of concentric outer layer portions (α layer) stained with ruthenic acid and an inner portion (β layer) not stained with ruthenic acid,

(b) the inner layer portion (β layer) not stained with ruthenic acid has dispersed therein microscopically a multitude of portions (γ layer) stained with ruthenic acid, and

(c) the average particle size of said β layer is 1,500 to 2,500 Å, the average thickness of the α layer surrounding said β layer is 250 to 400 Å, and the average particle size of the island as a whole is 2,000 to 3,000 Å, and when said thermoplastic acrylic resin composition is fractionated with acetone,

(d) the portion soluble in acetone occupies 30 to 98% by weight of the composition and comprise 80 to 100% by weight of methyl methacrylate units, 0 to 20% by weight of alkyl acrylate units, in which the alkyl group has 1 to 8 carbon atoms, and 0 to 20% by weight of vinyl monomer units copolymerizable therewith, and

(e) the portion insoluble in acetone is 2 to 70% by weight and comprise 20 to 70% by weight of methyl methacrylate units, 10 to 75% by weight of alkyl acrylate units, in which the alkyl group has 1 to 8 carbon atoms, and 2 to 30% by weight of vinyl monomer units copolymerizable therewith, wherein the swelling index of said acetone-insoluble portion in methyl ethyl ketone is 1.5 to 6, and the tensile modulus is 1,000 to 10,000 kg/cm².

2. The thermoplastic acrylic resin composition according to Claim 1, wherein the average thickness of α layer is 300 to 400 Å.

3. The thermoplastic acrylic resin composition according to Claim 1, wherein the swelling index of the portion insoluble acetone in methyl ethyl ketone is 2 to 4.5, and the tensile modulus is 2,000 to 6,000 kg/cm².

4. A thermoplastic acrylic resin composition according to claim 1, substantially as described in any one of the Examples.